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The Raman spectrum from pure silica optical fibers has been analyzed into a set of Gaussian components. Each component used is related to an observed feature of the spectrum, and a residual of about 1% resulted without the use of additional components. Both single- and multi-phonon peaks were fitted. These Gaussian components have analog in the infrared absorption spectrum, and hence they are of value in studying the fundamental and overtone infrared absorption of silica, as well as the infrared OH overtone and combination spectra.

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"Model Analysis of the
Raman Spectrum from
Fused Silica Optical Fibers"

by

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ABSTRACT

The Raman spectrum from pure silica optical fibers has been analyzed into a set of Gaussian components. Each component used is related to an observed feature of the spectrum, and a residual of about 1% resulted without the use of additional components. Both single- and multi-phonon peaks were fitted. These Gaussian components have analogs in the infrared absorption spectrum, and hence they are of value in studying the fundamental and overtone infrared absorptions of silica, as well as the infrared OH overtone and combination spectra.

INTRODUCTION

The Raman spectrum of fused silica is useful in elucidating its infrared absorption spectrum. Because the near-infrared absorption in silica fibers arises from overtones, combination tones, and tails from the fundamental infrared, an understanding of the silica infrared spectrum is of importance in determining the basic limits to transmission in optical fibers. By studying the Raman spectrum, features which may be weak and uncertain in the infrared can be confirmed. Even the important OH overtone absorptions include combinations involving silica infrared fundamentals. In a recent study of the OH overtone structure using a technique of Gaussian decomposition of the overtone absorption contours,[1] it was necessary in order to obtain consistent overtone structures, to invoke combination tones between OH overtones and silica infrared fundamentals which are relatively weak and unclear.

In this work we have used a similar analytical technique to resolve the Raman spectrum of fused silica (intensified by using long optical fibers) into a set of Gaussian components. This was accomplished using the strict constraint that only components correlated with a feature in the spectrum such as a peak, a shoulder, or a foot were employed. The resultant decomposition provided relative amplitudes and widths of the components. We have found that the Raman region between 0 and 900 cm^{-1} could be fitted with a residual of 1% using only 10 components. One interesting result of this fit is that a weak fundamental infrared component used in explaining part of the OH overtone absorption spectrum was confirmed.[1] In the present work this component is a major one, despite the fact that it appears only as a shoulder in the Raman spectrum.

Previously there has been only one attempt at decomposing the Raman contour from fused silica using a set of parabolas.[2] However, a different view of the structure of the Raman contour has generally prevailed. Theoretically, the depolarized Raman contour, when corrected for the Bose-Einstein thermal population factor, is the product of the density of states times the frequency dependent coupling coefficient, which involves Raman matrix elements.[3-5] The only reported computer decompositions using Gaussian components for fused silica have involved OH-stretching contours related to impurity OH.[6,7]

In the present work we applied Gaussian computer decomposition directly to the fundamental Raman spectrum from a pure (undoped) fused silica optical fiber, clad with silicone rubber, and 100 μm in diameter.[8] The rationale for this procedure depends partly upon its success, although some justifications for it have been reported.[7] Of course, the use of components does not at all imply that the density of states view is incorrect. On the contrary, the present approach is seen as a possible method of subdividing the density of states according to specific contributions.

RESULTS AND DISCUSSION

In the present work the Raman spectrum from long fused silica optical fibers[9] was transferred to a straight horizontal baseline and deconvoluted using a DuPont 310 analog computer. The spectrum of fused silica and the results of our computer modelling of it are shown in Fig. 1 for the Raman region between 0 and 900 cm^{-1}.

In Fig. 1 the Raman spectrum from a pure fused silica optical fiber is shown in the upper spectrum, (a). The Gaussian components used to model it are shown below in (c). Each Gaussian component correlates by number (1 to 10) to the corresponding feature in the Raman spectrum. The total integrated residual of the fit, using only Gaussian components corresponding to observed experimental features is negligible, 1%, as is the running residual shown graphically in (b) of Fig. 1.

From Fig. 1 it is evident that the component centered near 235 cm^{-1} correlates with the weak shoulder near 280 cm^{-1}. The 280 cm^{-1} shoulder has been reported several times, e.g., Refs. (2,10,11). This feature corresponds to the infrared fundamental frequency which was invoked recently in explanations of the OH overtone structure.[1] The integrated intensity of the 235 cm^{-1} component is 67 % of the integrated intensity of the most intense component at 370 cm^{-1}, given a relative integrated intensity of 100 in Table I. The 235 cm^{-1} component is thus the third most intense Raman component in the fused silica spectrum, which strongly supports the recent infrared combination assignments.[1] (It should

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Fig. 1. Gaussian computer deconvolution of the Raman contour from fused silica. (a) Raman contour from Ref. (9) after transferral to horizontal baseline, (b) the running residual, sum of Gaussian components minus experimental Raman amplitude, and (c) the Gaussian components. Same amplitude scale for (a), (b), and (c).

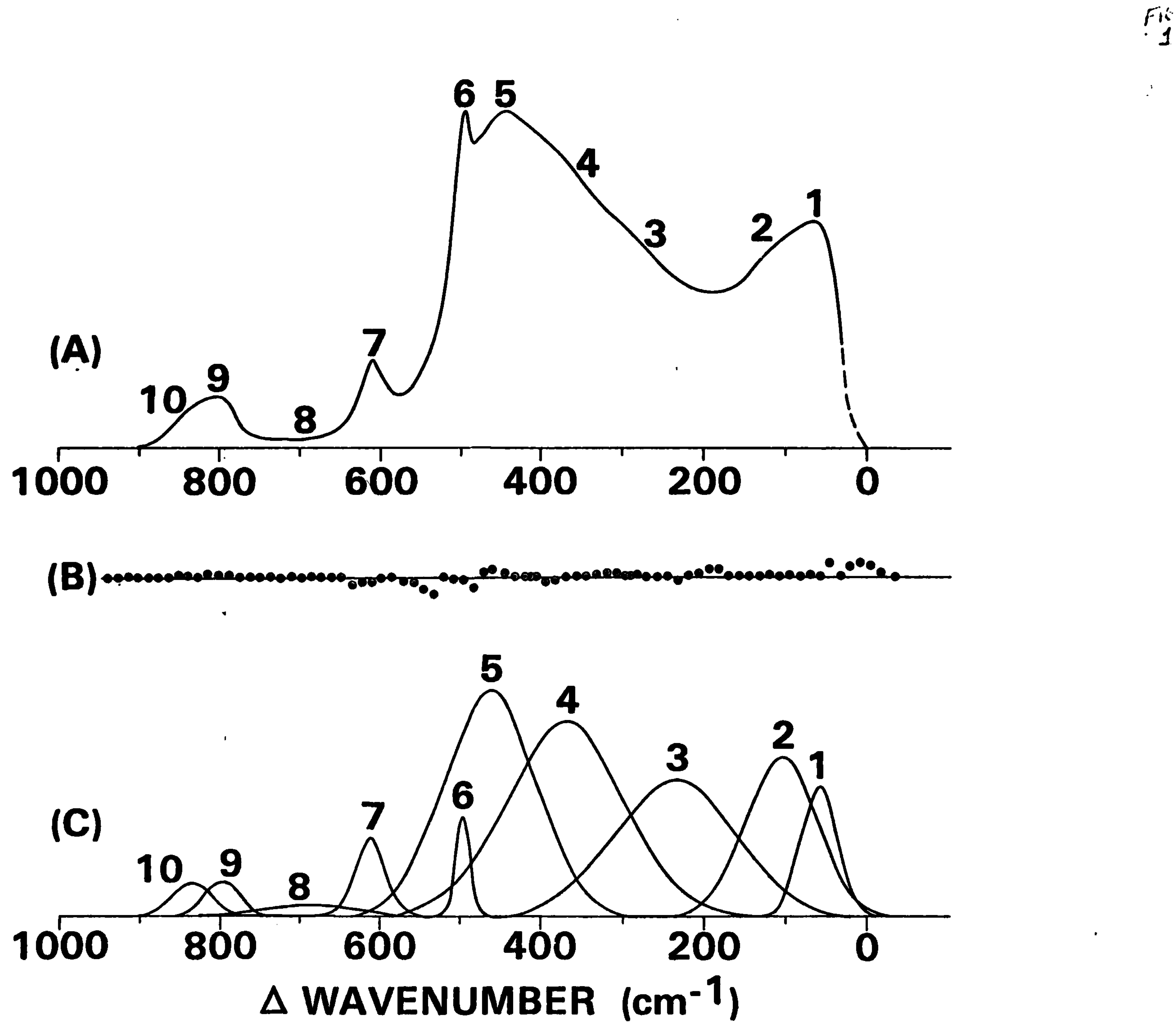

Fig. 1
(A)
(B)
(C)
1
2
3
4
5
6
7
8
9
10
1000
800
600
400
200
0
Δ WAVENUMBER (cm-1)

be noted that the 280 cm^{-1} shoulder correlates with a Gaussian component whose center is shifted to 235 cm^{-1}. However, the present correlation does not require that the observed and computed features have exactly the same frequency.)

In addition to the unexpected intensity of the 235 cm^{-1} component, it is noteworthy that the intensities of two other components at 105 and 370 cm^{-1}, which also correspond to Raman shoulders, are surprisingly large. Furthermore, the peak Raman intensity near 430 cm^{-1} does not correspond to the strongest, but rather to the second strongest component at 460 cm^{-1}, having a relative integrated intensity of 85, Table I.

We next extended the Gaussian computer analysis to Raman regions not shown in Fig. 1, namely, to 2600 cm^{-1}.[12] As before we demanded a strict correlation between features observed, and Gaussian components employed. Again good results were obtained with negligible residuals. The results of the computer analysis are given in Table I.

The Raman bands listed in Table I below either 1055 or 1180 cm^{-1} refer primarily to one-phonon or fundamental vibrations, and the multi-phonon overtone and combination region extends from either 1180 or 1460 cm^{-1} to 2600 cm^{-1}, or above.[12] (It is uncertain whether the 1180 cm^{-1} band is a one- or two-phonon vibration.)

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Table I. Parameters obtained from Gaussian computer deconvolution of the Raman spectrum from fused silica optical fiber. Most intense component given a value of 100, second column. Components above 830 cm^{-1} from spectra of Refs. (9,10).

TABLE I

Component Position (cm^{-1})	Relative Integrated Intensity	Half width (cm^{-1})
55	20	55
105	50	110
235	67	185
370	100	175
460	85	140
495	8	25
610	10	45
685	5	155
795	5	55
830	6	60
900	1	--
1055	3	70
1180	3	100
1460	--	140
1605	--	140
2015	--	100
2150	--	150
2305	--	115
2405	--	160

The tails of the multi-phonon components at 2015, 2150, 2350, and 2405 cm^{-1}, Table I, extend from about 1950 to 2600 cm^{-1}. This spread covers the infrared absorption region in fused silica for which bands between 3.8 and 5.1 μm[13] have been reported and assigned to two-, three-, and four-phonon combinations of silica fundamentals. In the region above 2.0 μm, the transmission loss of doped silica fibers is known to increase by several orders of magnitude because of multi-phonon combinations involving silica fundamentals.[13-15] Hence, the present Gaussian analysis may be of use in understanding high loss mechanisms in optical fibers.

In summary, we have used a new approach in the analysis of the Raman spectrum of fused silica, namely, decomposition into a set of Gaussian components, each of which is related to a known feature of the vibrational spectrum. This decomposition yields the relative amplitudes and widths of the components. Some components which are weak in the infrared spectrum, and poorly resolved in the Raman spectrum, are shown to be major components in this analysis. This finding confirms the inference made previously[1] that these components contribute to combinations which are part of the OH overtone absorption spectrum of silica glass.

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